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Hydrometallurgical Processing of the Wastes of Polymetallic Ore Dressing

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Abstract

The possibility of hydrometallurgical treatment of old flotation tailings to extract base and noble metals was investigated. Two samples of old flotation tailings samples containing 0.26% and 0.36% of copper, and 0.22% and 0.23% of zinc were the subjects of this study. Agitation and percolator leaching was performed with distilled water and sulfuric acid solutions (of 0.5 to 10% H_2SO_4). It was shown that under certain conditions (sulfuric acid concentration) it was possible to achieve selective leaching of non-ferrous metals and obtain solutions with relatively low concentrations of iron ions, which is necessary for further effective extraction of non-ferrous metal ions from the solution. The effect of acid leaching on further gold recovery from the first sample containing 0.7 g/t of gold by cyanidation was investigated. The sample of the tailings after leaching with a 1% sulfuric acid solution was leached with 10% sulfuric acid. After that, the tailings sample and the acid leach residues were subjected to sorption cyanidation. Two-stage acid leaching with 1 and 10% sulfuric acid provided the higher gold recovery than one-stage (49 and 65%, respectively). Also it was shown that pregnant solution obtained during leaching of the second sample with 10% sulfuric acid may be used for oxidative leaching of substandard copper-zinc concentrate that allowed to 13 and 48% of copper and zinc from the concentrate during the leaching at 80°C.

Keywords: flotation tailings, leaching, substandard sulfide concentrates

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Non-ferrous metallurgy is one of the most important sectors for the Russian economy, and the country is the world leader in the extraction of some non-ferrous and precious metals, for example: in 2014, the Russian mining industry was second in the world nickel production (260 thousand tons), fifth in cobalt (6300 thousand tons), seventh for copper and lead (850 and 195 thousand tons, respectively), and eleventh for zinc (233 thousand tons) [1–3]. At the same time, the depletion of reserves of easily processed mineral raw materials, which can be treated using traditionally used technologies (flotation concentration, roasting, smelting, conversion), and many deposits, which are the raw material base for the most significant non-ferrous metallurgy enterprises, are largely depleted. The accumulation of a large amount of waste from ore mining, dressing, and metallurgical processing creates a high pressure on the environment, turning the territories around mining and processing integrated plants into an environmental disaster zone. Currently, the amounts of accumulated waste at many mining and processing integrated plants in Russia and the former USSR as well as the content of metals in them are not exactly known, since ore dressing wastes was often not accounted in the first half of the 20th century. According to different estimates, about 5 billion tons of overburden and 700 million tons of tailings are stored in dumps annually in the CIS countries. In total, more than 40 billion tons of waste was accumulated in the dumps of mining enterprises of the Russian Federation [4]. Russian researchers agree that these storages negatively affect the environment, primarily through pollution of surface and groundwater and, as a result, soil [5, 6]. The gradual depletion of high-garde ore deposits leads to the fact that storage facilities for metallurgical production waste are beginning to be regarded as technogenic deposits of valuable (non-ferrous and noble) metals. Despite this, the involvement of wastes of dressing and metallurgical production in the economy is limited due to the lack of effective technologies for their processing.

The goal of this work was to study the process of leaching old flotation tailings of polymetallic (copper-zinc) ores of Ural deposits with sulfuric acid solutions of various concentrations to determine the technological feasibility of selective leaching of non-ferrous metals from dressing wastes, as well as obtaining ferric iron solutions that can be used for oxidative leaching various mineral raw materials. In our previous studies, it was shown that these samples of flotation tailings can be bioleached, however, the resulting pregnant solutions were characterized by a high content of ferrous and ferrous ions (10-15 g/L) and low concentrations of non-ferrous metals (0.3–0.45 g/L), which hindered the further extraction of non-ferrous metals from the liquid phase [7, 8]. In addition, it was shown that sulfuric acid leaching can make it possible to obtain productive solutions with high concentrations of Fe^{3+} ions from samples of old tailings, which are a strong oxidizing agent and can be used to leach non-ferrous metals from various raw materials, including slags and wastes of their processing [9].

The metal content in the samples of flotation tailings is shown in Table 1. Fraction of particles -74 μm was 95% (P_{95} = 74 μm). Samples of flotation tailings were characterized by a high iron content in the form of pyrite and oxide minerals.

Table 1: The content of iron and non-ferrous metals in the samples of old flotation tailings.

Sample	Fe_{total}, %	Cu,%	Zn, %
1	17.4	0.26	0.22
2	23.2	0.36	0.23

Non-ferrous metals were leached from samples of old flotation tailings using sulfuric acid solutions (from 0.5 to 10%) or distilled water. Leaching was carried out in percolators and on a bottle agitator. For percolation leaching, 100 g of old tailings were loaded into percolators, and 100 mL of acid solutions or 100 mL of water were used as leaching solution. During agitation leaching, the pulp density (S : L) was 1 : 5, and the leaching time was 3 hours.

The experimental results are presented in Figures 1 and 2. Percolator leaching made it possible to extract from the first sample up to 43 and 47% of Cu and Zn, respectively. The recovery was maximum when leaching with 1 and 2.5% sulfuric acid solutions. During agitation leaching, the maximum leaching rate was reached with 2.5% sulfuric acid solution (52 and 54% Cu and Zn), but the rate of leaching with all solutions, as well as with distilled water, did not differ significantly. Percolator leaching made it possible to leach from the second sample of tailings up to 54 and 37% Cu and Zn, while agitation allowed to extract up to 34 and 68% Cu and Zn, respectively. The rate of extraction of non-ferrous metals from the second sample during leaching with water did not differ significantly from that reached with acid solutions. In all variants of the experiment, an increase in the sulfuric acid concentration led to an increase in the concentration of iron ions in pregnant solutions, which impedes the extraction of non-ferrous metals from the solutions. Thus, it was shown that under certain conditions it is possible to achieve selective leaching of non-ferrous metals and to obtain solutions with relatively low concentrations of iron ions, which is necessary for further effective extraction of non-ferrous metal ions from solution.

Since the first sample of the tailings contained 0.7 g/t of gold in addition to copper and zinc, further studies were carried out to extract gold from this sample of waste. The effect of acid leaching on further gold recovery by cyanidation was investigated. Flotation tailings subjected to percolator leaching with 1% sulfuric acid, since in this variant optimal values were achieved for the selective extraction of non-ferrous metals, was used for further research. A sample of the tailings after leaching with a 1% sulfuric acid solution was leached with 10% sulfuric acid. After that, the tailings sample and the acid leach residues were subjected to sorption cyanidation (cyanide concentration 1 g/L, 48 hours). The results are shown in Table 2.

Table 2: Gold recovery by cyanidation from a flotation tailings sample and acid leaching residue

Product	Au recovery, %
Old flotation tailings	50
Residue after the leaching with 1% sulfuric acid	49
Residue after the leaching with 1% and 10%	65

Two-stage acid leaching with 1 and 10% sulfuric acid provided the highest gold recovery, probably due to the removal of oxide minerals, which was necessary for cyanidation.

With the second sample of the tailings, further studies were carried out on the agitation leaching of non-ferrous metals and the preparation of a solution of ferric ions, since leaching of the solution resulted in solutions with higher concentrations of ferric ions. For this purpose, studies on a two-stage agitation leaching of a tailings sample at a pulp density of S : L = 1 : 2.5 were conducted. In the first stage, leaching was carried out with distilled water, and in the second, with 10% sulfuric acid.

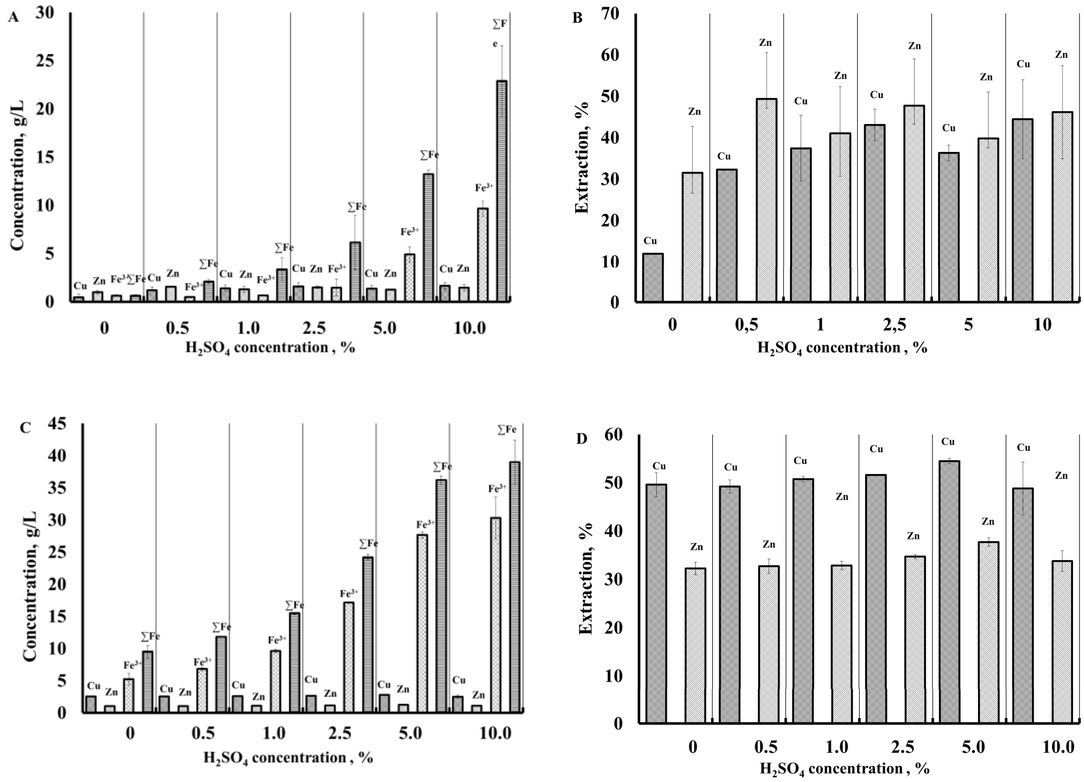

Figure 1: The concentration of metal ions in pregnant solutions of percolator leaching and the rate of leaching of copper and zinc. A and B - the first sample, C and D - the second sample of flotation tailings.

The content of metal ions in the pregnant solutions of the first and second stage after 3 hours of leaching is shown in Table. 3. It was shown that at a higher pulp density, the rate of leaching of copper and zinc in the first stage was approximately the same as at S : L = 1 : 5 (31 and 64%, respectively). At the same time, the second leaching stage practically did not allow to extract an additional amount of non-ferrous metals, but it allowed to obtain a solution containing about 11 g/L Fe^{3+}.

Table 3: The content of iron and non-ferrous ions in pregnant solutions of two-stage leaching

Stage	Fe^{3+}, g/L	Fe^{2+}, g/L	Cu^{2+}, g/L	Zn^{2+}, g/L
1 (leaching with water)	0.7875±0.04	0.7±0.06	0.4575±0.01	0.589±0.02
2 (leaching with 10% H_2SO_4)	11.27±0.56	0.665±0.12	0.06375±0.003	0.04775±0.001

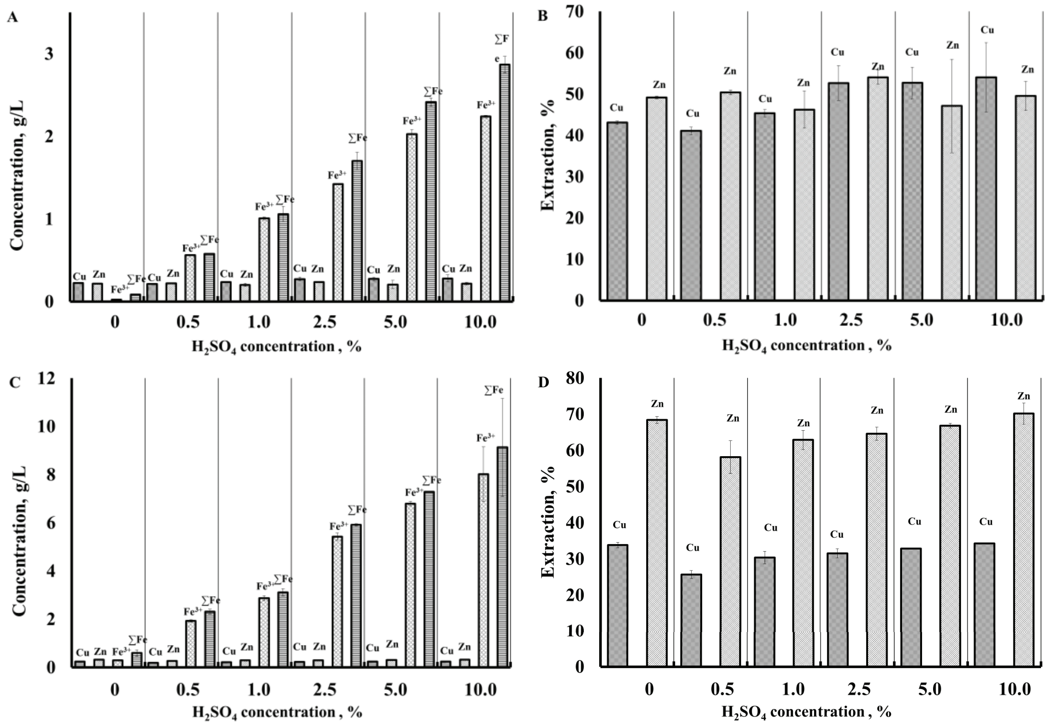

Figure 2: The concentration of metal ions in pregnant solutions of agitation leaching and the rate of leaching of copper and zinc. A and B - the first sample, C and D - the second sample of flotation tailings.

An experiment on leaching non-ferrous metals from substandard copper-zinc concentrate containing 16 and 5.3% copper and zinc was carried out with a pregnant solution of the second stage of acid leaching of the old tailings.

The concentrate was leached at 80°C for 3 h at S: L 1: 10. It was shown that at 80°C of Fe^{3+} ions concentration in the solution decreased over three hours to approximately 2.45 g/L, which indicates that ferric ions were reduced to Fe^{2+} ions during oxidative leaching (the concentration of Fe^{2+} ions increased up to 14 g/L). The oxidative leaching led to the release of iron, copper and zinc contained in the concentrate into the liquid phase. It was possible to extract about 14% copper and 47% zinc into the solution for 3 hours. Thus, it was shown that a productive solution of acid leaching of flotation tailings can be successfully used for oxidative leaching, for example, substandard copper-zinc concentrates, from which excess zinc can be removed using hydrometallurgical methods.

The results of this work demonstrated that for the processing of old tailings containing valuable metals, effective hydrometallurgical methods can be developed to achieve not only a high degree of metal recovery, but also high selectivity. At the same time, acid leaching can not only allow the extraction of non-ferrous metals, but also increase the degree of gold extraction and obtain productive solutions containing high concentrations of ferric ions, which can be used to leach other types of raw materials.

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